A

Ph.D. Synopsis in the subject of Physics

on

"Studies on Co and Fe doped CuO thin films prepared via chemical route"

Submitted to

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SEPTEMBER-2023

1. INTRODUCTION

Nanoscience is an interdisciplinary subject. Physicist Richard Feynman first proposed the notion of Nano by sharing his desire to build things on smaller dimensions. The idea is to create nanoscale machines to manipulate, control to the atomic size. Nanotechnology has been defined as being concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size [1]. Nanotechnology has profoundly transformed science and plays a worthy role in several innovative aspects of the new millennium. The synthesis of nanomaterial can make a significant contribution to international efforts sustainability. It is a wide field of research and development that has grown rapidly in recent years around the globe. Nanotechnology enables scientists and engineers to understand and control matter at the nanoscale level, allowing them to manipulate materials with unique properties and behaviours. By harnessing these properties, researchers can develop new materials, devices, and systems with enhanced functionalities and performance. Nanomaterials have at least one dimension between 1 and 100 nanometres [2]. A nanometre (nm) is 10^{-9} meter. At this nanoscale level, material shows very distinct properties that of the larger scale. It is widely assumed that the catalytic performance, physical and chemical properties of nanostructured materials are mediated by their sizes and shapes, composition and structures.

In recent years, metal oxide thin films have attracted much attention owing to interest in research due to their unique physical and chemical properties. It is a gateway to the future for human beings on Earth, leading to paid attention to modifying the nanostructured materials via synthesis and fabrication methods. The metal oxide thin films are among the widest-used manufactured thin films because of their unique properties including thermal and chemical stability, flexibility, durability, easily accessible, environment friendly, and simplicity when manufactured. Such properties of thin films make the nanophase structures indispensable tools in modern nanotechnology.

Metal oxide at nanoscale are promising materials for the next generation of gas sensor device applications, because of its high sensitivity, excellent stability and simplicity. The metal oxides include WO_3, SnO_2, ZnO, CuO, TiO_2 [3]. Among all these, CuO is one of the materials whose properties can be easily tuned due to its bandgap of 1.4eV which also havepotential applications in solar cell, catalysis's, optics and gas sensor. Synthesis techniques wereemployed in past decades to prepare pure and doped CuO thin films includes spray pyrolysis, sputtering, SILAR, dip coating, CBD etc [4]–[6].

Moreover, CuO has been also wide range of applications including health care, cosmetics, chemical industries, electronics, industries, optoelectronics, catalysis, single electron transistors, light emitters, nonlinear optical devices, spintronics, and photo-electrochemical applications [7], [8]. It is a p-type semiconductor material having a monoclinic crystal structure in nature. Copper oxide has two common stable forms as copper oxide (I) or cuprous oxide Cu_2O (cuprite phase) and copper oxide (II) or cupric oxide CuO (tenorite phase). The copper oxide (I) has a cubic structure, with optical band gap values of 2.1-2.6eV. The Copper Oxide (II) has a monoclinic structure and has band gap values of 1.3-2.1eV. It possesses a narrow band gap of ~1.2eV making it a most fascinating multifunctional material [9], [10].

Doping has a significant impact on the structural, optical, and electrical structure of materials and hence it enhances of properties of the materials and is suitably used in the field of gas sensing, solar cell, and electrochemical applications [11]–[13]. Dopant can change structure, morphology, and the optical properties which creates more active centers at grain boundaries, and produce defects [14]. A strategy has been advanced to alter properties by doping group III elements in metal oxide thin films. Among all the elements Co and Fe are very rarely studied for the doping with CuO thin films.

2. LITERATURE SURVEY

Majibul Babu et al. **[7]** reported that the effect of Co doping on the structural, morphological and optical properties of CuO thin films were investigated. The nature of synthesized CuO thin films were confirmed using hall measurements. The investigation results suggests that 8 at. % of CuO thin films may have potential application in the field of spintronic and optoelectronic devices.

Fatima Zahra et al. [15] prepared pure CuO and **Fe-doped CuO** nanostructured thin films by using spray pyrolysis technique at 350^{o}C. The prepared films were examined using x-ray diffraction, field emission scanning electron microscopy and uv-visible spectrophotometer. The significant change in hall effect measurements were observed. The resistivity increases and the carrier mobility decreases with increasing Fe concentration.

Muhammed G. et al. [16] investigated the effect of Ni doping on the structural, optical and morphological properties on CuO thin films. Moreover, the H_2 gas sensing characteristics of pure and Ni-doped ZnO thin films were analyzed.

Debashrita Mahana et al. [17] synthesized CuO thin films using RF sputtering and the effect of deposition temperature on gas sensing properties was examined. Moreover, the structural, morphological, and optical properties were reported. The formation of different phases of copper oxide was observed.

R. Daira et al. [17] reported the preparation of nano-sized CuO thin films by chemical spray pyrolysis and presented characterization results obtained from the variation of the band gap energy as a function of the crystallite size. The decrease of the band gap energy as a function of the increasing crystallite size was explained by the quantum confinement effect.

S.K. Shinde et al. [18] demonstrated that the surface morphology and electrochemical supercapacitive properties of materials are dependent on the deposition temperature of CuO thin films prepared by the spray pyrolysis technique. The significant improvement observed in the supercapacitor properties was attributed to the particle size and polycrystalline structure of the CuO thin films. Results support that the CuO thin films can be suitable candidates as electrode materials for supercapacitor applications.

Abderrahim Moumen et al. [19] observed the crystallinity improvement as increasing the temperature from 300 to 375°C. he prepared films were studied for gas sensing studies. A low-cost acetone sensor at 375^{o} C showed a response of 33%, with response and recovery time of 160 and 360s, respectively.

V. Jagadeesan et al. [20] observed the effect of different Molarities (0.1, 0.2 and 0.3) of CuO thin films on structural, optical, and morphological properties. The crystallite size of CuO thin films was found to increase from 13 to 23nm. The optical band gap reduced from 2.1 to 1.8eV with an increase in molar concentrations. The prepared films were studied for electrical measurements.

David Prabu et al. [21] prepared various thin films with variation of deposition temperature of 250 to 300 °C. All the prepared films possess single cubic crystal structure phase of cuprous oxide (Cu_2O) whereas the films deposited at 310 and 320°C were found to have a mixed phase of CuO and Cu_2O. Above 310°C the Cu_2O phase become unstable and started to convert as CuO with cluster formation of particles. Bandgap decreases from 2.44 to 1.97eV.

Muthukrishnan et al. [10] prepared thin films by spray pyrolysis in the range of 250 to 500°C deposition temperatures. The prepared films were polycrystalline in nature exhibiting a monoclinic structure. It is found that the optical absorbance decreases with the increase in

temperature. Hall measurement system shows that the copper oxide films are p-type semiconductors with carrier concentration in the order of 10^{16} cm^{-3}.

Chetoui Abdelmounaïm et al. [22] have exposed the effect of molarity on structural, optical, morphological and gas sensing properties of copper oxide films deposited by spray pyrolysis method. The gas sensing measurements confirm that this porous surface structure is the most sensitive to different CO_2 concentrations.

Table: CuO thin films for gas sensor applications

CuO thin film	Gas	Temperature (°C)	Response time (sec)	Recovery time (sec)	Concentration (ppm)	Ref.
La-doped CuO	NO_2	350	15.74	4.01	-	[4]
CuO	C_2H_5OH	250	-	-	100	[23]
CuO (Annealing time)	NO_2	400	3.78	1.04	15	[24]
CuO	NO_2	200	20.57	235	100	[25]
Pb-doped CuO	H_2	300	10	50	1000	[26]
CuO (Molar concentration)	CO_2	350	10	6	100	[22]

Literature review results demonstrate that, CuO thin films can be suitable candidate for solar cell, sensing and supercapacitor applications. **Co** and **Fe** are recommended to be used as dopant elements since they can make significant modifications in the host CuO properties that qualify it for new applications.

3. STATEMENT OF PROPOSED PROBLEM

The systematic deposition and characterizations of pure and doped films will be discussed in detail for various applications. Doping of Co and Fe into CuO has not been studied very thoroughly for application purposes till now. The present work focuses on the synthesis of Co and Fe-doped CuO thin films to study gas sensing properties. The aim of this work is to minimize the operating temperature and to develop a sensor operating at lower temperatures. The synthesis of films will be carried out so as to detect minute traces of gases as well as to lower the operating temperature.

4. AIM AND OBJECTIVES

The main goal of our research work is to develop novel Co and Fe-doped CuO thin films to investigate their significant gas-sensing characteristics. In this work, we proposed to have improved structural, morphological, and optical properties by doping of Co and Fe transition metals. Investigations in order to explore the research studies that facilitate the innovative work of new materials.

- To optimize deposition parameters.
- To synthesize pure, **Co**-doped, and **Fe**-doped **CuO thin film** by chemical route method.
- To analyze the effect of Co and Fe doping on CuO thin films through structural, optical, and morphological properties.
- To study the gas sensing characteristics of the pure and doped CuO thin films.

5. MOTIVATION

CuO is one of the thermally and chemically stable metal oxide widely studied in the field of research. It is a p-type material and exhibits unique physical and chemical properties which makes it suitable in the field of sensor devices. The structural, morphological and optical properties of the CuO thin films can be modified using a suitable dopant. In the present work,we propose the doping of Co and Fe. Pure and doped CuO thin films will be prepared using chemical methods and will be evaluated to study the effect of doping. The pure and doped CuO thin films are suitably used in the field of solar cells, supercapacitors, sensing devices and medical applications.

6. HYPOTHESIS

The research work is directed to prepare novel **Co** and **Fe-doped CuO** thin films. In this work, we propose to improve the properties of pure CuO thin films by doping. The effect of structural parameters and morphological studies will be investigated. The prepared films are expected to show enhanced performances in the field of applications such as gas sensing, solar cell, and supercapacitor performance etc.

7. RESEARCH METHODOLOGY

a. Thin Film Deposition:

To synthesize pure CuO, Co and Fe doped thin films via Chemical route.

b. Characterization techniques:

- **Structural properties**

The structural properties of the prepared samples will be investigated by using X-ray diffractiontechnique **(XRD)**. The crystal structure and purity of the phase will be confirmed using XRD.

- **Morphological and compositional studies**

The morphology of the prepared sample will be examined by field emission scanning electron microscopy **(FESEM)**. The obtained morphologies and its relevance in various field of applications. The composition of the synthesized films will be evaluated using energy dispersive x-ray analysis **(EDAX)**.

- **Optical properties**

The optical properties of the prepared films will be studied using **UV-Visible spectrophotometer**. The optimized properties will be evaluated for the optoelectronics device applications

- **Gas sensing studies**

The prepared films will be characterized to study the gas sensing properties using **Keithley electrometer**.

8. CHAPTER SCHEME

- Chapter 1: Introduction
- Chapter 2: Experimental and characterization techniques
- Chapter 3: Synthesis, characterization and gas sensing properties of Co-doped CuO thin films

- Chapter 4: Synthesis, characterization and gas sensing properties of Fe-doped CuO thin films
- Chapter 5: Conclusion and future work plan

9.YEAR WISE PLAN OF WORK

First-year

- Coursework
- Literature review
- Synthesis and optimization pure CuO thin films

Second year

- Synthesis of Co and Fe-doped CuO thin films
- Structural Characterization of prepared thin films will be studied
- Surface morphology and optical properties of the prepared samples will be studied.
- The prepared films will be evaluated for applications.
- Work will be presented at national/international conferences.

Third year

- The research data will be published in a reputed national/ international journal.
- Submission of the thesis of proposed work for the Doctoral degree.

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